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A MEMORANDUM REPORT: PHYSICAL CONSTANTS OF MCE

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CHEMICAL WARFARE SERVICE

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This report was originally published on 16 July 1945 by the Chemical Warfare Service (Edgewood Arsenal, MD) as T.D.M.R. 1094 (Control No. 5004-1094). The report is being republished with two corrections: the first correction is in Table 2 on page 3 and the second correction is on page 5 of the text.

14. ABSTRACT-LIMIT 200 WORDS
The object of Project A 1.13, Agent MCE and Related Compounds, is to study MCE and MFI and their analogs with a view to estimating their effectiveness as CW agents. The object of the work described in this report was to measure the various physical constants of MCE, particularly the vapor pressure-temperature relationship, in order to make these data available to investigators working on the various phases of this project.

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MCE, Vapor pressure, Volatility, Heat of vaporization, Density, Clausius-Clapeyron equation, Surface tension, Viscosity, Freezing point, GA

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ABSTRACT

Object:

The object of Project A 1.13, Agent MCE and Related Compounds, is to study MCE and MFI and their analogs with a view to estimating their effectiveness as CW agents.

The object of the work described in this report was to measure the various physical constants of MCE, particularly the vapor pressure-temperature relationship, in order to make these data available to investigators working on the various phases of this project.

Results:

The physical constants of MCE are as follows:

n_D^{20}	1.4240
Formula weight	162.3
Parachor (25 °C.)	359.8
Freezing point (purest sample)	–50.0 °C.
Boiling point (extrapolated from vapor pressure data)	246 °C.
Heat of vaporization average values 35–95 °C.	12900 cal./mol. or 79.6 cal./gram.

Temp. °C.	Vapor Pressure mm. Hg	Volatility mg./l.	Density g./ml.	Viscosity		Surface Tension dynes/cm.
				centistokes	centipoises	
–10			1.105			
0			1.096			
10			1.087	3.00	3.26	
15			1.082			
20	0.0483	0.429	1.077			
25	0.0701	0.612	1.073	2.19	2.35	32.0
30	0.100	0.858	1.068			31.8
35	0.142	1.20	1.064	1.67	1.78	
45	0.275	2.25				

The vapor pressure - temperature relationship is as follows:

$\log_{10} p = 8.305 - \frac{2820}{T}$ where p = vapor pressure, mm. Hg.
T = temperature, °K.

The expansion to 65 °C., and the density of crude MCE tapped from a 250 kg. bomb, were measured, and are in Table 4.

Conclusions None.

Recommendations: None.

PREFACE

The work described in this report was authorized under project no. A 1.13. The work was started in May 1945 and completed in July 1945.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

Acknowledgments

David E. Tevault (Joint Research and Development, Inc., Belcamp, MD) and Ann Brozena (U.S. Army Edgewood Chemical Biological Center) identified and corrected two errors in the original 1945 publication.

Note from Reviewers

This version is a reprint with corrections of Harris, B.L. *A Memorandum Report*: *Physical Constants of MCE*; T.D.M.R. 1094; Chemical Warfare Service: Edgewood Arsenal, MD, 1945; SECRET Report (ADB964103).

The purpose of this report is to correct two technical errors recently found in T.D.M.R. 1094. The first error appears to be a transcription error for the vapor pressure value listed in Table 2 (page 3 of original report) for the last vapor pressure value reported at 25 ºC. That value is listed in Harris' notebook as 0.0433, but was listed in Table 2 as 0.433. A more obvious and potentially significant error was found in the reporting of the Clausius-Clapeyron correlation. The A value was reported to be 8.307 twice on page 5 of the original report but 8.305 elsewhere in the same report. Harris' notebook contains the original data analysis, which indicates that the value is 8.305.

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A MEMORANDUM REPORT: PHYSICAL CONSTANTS OF MCE

1. INTRODUCTION

1.1 Object

The object of Project A 1.13, Agent MCE and Related Compounds, is to study MCE and MFI and their analogs with a view to estimating their effectiveness as CW Agents.

The object of the work described in this report was to measure the various physical constants of MCE, particularly the vapor pressure - temperature relationship, in order to make these data available to investigators working on the various phases of this project.

1.2 Authority

The authority for the work described in this report is Project A 1.13 of the Project Program for Fiscal Year 1946.

2. HISTORICAL

Early in the spring of 1945 a number of captured German bombs and shell were received at Edgewood Arsenal. When one of each was tapped, both proved to contain crude MCE. The bomb was the 250-kg. size, and contained MCE with approximately 5% of monochlorobenzene. The shell (105-mm. howitzer) contained MCE with about 20% of monochlorobenzene. Samples of these materials were distilled by personnel in the Chemical Division to obtain the pure agent for study. Tests are now in progress on various phases of this study, and in order to supply background data for the testing and evaluation of the agent, the physical constants were determined and are reported here.

3. EXPERIMENTAL

3.1. Materials and Equipment

3.1.1 MCE

A number of samples of pure (twice-distilled) MCE and one sample of the crude material from the bomb were used in this work. In addition, one sample of material synthesized at this Arsenal by Capt. Rueggeberg (report in progress) was used. The results of analysis of the pure samples are given in Table 1.

Table 1. Analyses of Pure MCE Samples Used for Determinations of Physical Constants

	Calc.	Found				
Sample No.		M1063	M1067	M1078	M1081	S-184*
CN as HCN, %	16.04	16.07	15.78	15.45	16.19	16.23
Nitrogen, %	17.28	16.98	17.00	16.65	16.78	17.05
Phosphorus, %	19.10	19.04	19.04	19.12	18.76	–
n_D^{20}	–	1.4239	1.4243	1.4239	1.4240	1.4240
n_D^{30}	–	1.4190	1.4185	1.4197	1.4200	–
Chlorine	–	–	–	–	0.12	nil

*This sample was synthesized at Edgewood Arsenal. The others were material twice distilled from that in the 250-kg. bomb.

3.1.2 Equipment

The equipment is described under the separate tests in Section 3.3 below.

3.2 Procedure

The various procedures are described in Section 3.3, below.

3.3 Results

3.3.1 Vapor Pressure, Volatility, and Heat of Vaporization

3.3.1.1 Transference Method

The vapor pressure was measured at 25 – 55 °C. in a vapor-transference apparatus, by bubbling nitrogen at measured pressure through the agent in a triple-pass bubbler immersed in a water thermostat. The procedure has been described in detail in numerous reference texts. The specific apparatus and its manipulation have been completely discussed by Pecorella and Macy (*1*). The values obtained at first were erratic, due to the difficulty of weighing the small quantities evaporated as a result of the low vapor pressure of the agent and the short time of the run, and so were discarded. The later values were obtained by allowing the apparatus to run for 2 to 4 days at a time but even so the values at 25 °C were not consistent. The experimental values so obtained are given in Table 2. Two samples of MCE were used for the determinations, which are corrected to mm. of Hg. at 0 °C.

Table 2. Experimental Values of Vapor Pressure of MCE by the Air Transference Method

				Vapor Pressure		
Temp. (°C)	Wt. Loss of MCE (g)	Vol. of Nitrogen (ml)	Pressure of Nitrogen (mm Hg.)	Sample M1063 (mm Hg)	Sample S-184 (mm Hg)	Average* (mm Hg)
25.0	0.0095	21980	760.0	0.0454		
	0.0137	25610	760.0	0.0561		
	0.0202	26640	760.6	0.0796		
	0.0118	28620	761.2	0.0433[a]		**
35.0	0.0287	20260	746.0	0.146		
	0.0292	20010	744.6	0.150		
	0.0236	17125	759.5		0.144	0.146
45.0	0.0235	9720	760.0	0.254		
	0.0342	14880	760.5	0.243		
	0.0505	21320	761.6	0.249		
	0.0342	11600	742.0	0.270		
	0.0257	10060	761.5		0.268	0.261
55.0	0.0355	6520	763.7		0.573	
	0.0385	8310	762.5		0.487	0.530

*The average values were obtained by averaging the determinations for each sample separately, and then averaging those values.

**No average was calculated due to the inconsistency of the data.

3.3.1.2 Ramsay-Young Method

This method is likewise a standard one described in a number of texts. The assembly of apparatus used for the work here was taken directly from Reilly and Rae (*2*). The essential feature was a thermometer, the bulb of which was wrapped with absorbent cotton kept wet with the agent by means of a dropping funnel, placed in an evacuated chamber immersed in a water thermostat. It was operated by evacuating the chamber to a measured pressure, allowing time for equilibrium, and reading the temperature. It was found that, due to the low vapor pressure of this agent, reliable results could only be obtained if the temperature and pressure were held constant for about an hour. Only two values were obtained by this method, as follows:

Temperature	Vapor Pressure
68.9 °C.	1.15 mm Hg.
93.3 °C.	3.7 mm Hg.

3.3.1.3 Distillation Data

The apparatus used by Rueggeberg to distill sample S-184 and one other only slightly less pure sample was one in which the manometer was connected to the point in the

[a] This value is incorrectly listed as 0.433 in TDMR 1094, but in Notebook 2363, Harris correctly lists it as 0.0433.

system at which the temperature was read. The distillation temperature-pressure data were, in effect, vapor pressure data, and are included in the values reported here as follows:

Temperature	Vapor Pressure
72.5–73 °C.	1.5 mm.
86–87 (mostly 87 °C)	3 mm.

3.3.1.4 Average Values of Vapor Pressure, Volatility, and Heat of Vaporization

The values reported above for the vapor pressure were averaged on a log p vs. 1/T plot by the method of least squares to give the following equation:

$$\log p = 8.305 - \frac{2820}{T}$$

where

log p = logarithm to the base 10 of the vapor pressure in mm. Hg.
T = absolute temperature, °K

The values calculated from this equation are given in Table 3. The check was quite good, as comparison with Table 2 or reference to the Figure will show.

The volatility of the MCE was calculated from the calculated values of vapor pressure by the ideal gas law and the values are given in Table 3.

The boiling point at atmospheric pressure (760 mm. Hg.) was likewise calculated from the equation above, assuming the plot of log p vs. l/T was linear to so high a value; the value so obtained was 246 °C.

Table 3. Vapor Pressure of MCE Calculated from the Experimental Data by Method of Least Squares

$$\log p = 8.305 - \frac{2820}{T}$$

Temperature (°C.)	Vapor Pressure (mm. Hg.)	Volatility (mg./l.)
20	0.0483	0.429
25	0.0701	0.612
30	0.100	0.858
35	0.142	1.20
45	0.275	2.25
246.3*	760	–

*Normal boiling point, assuming the equation holds to 760 mm. Hg.

The heat of vaporization was calculated from the modified Clapeyron-Clausius equation:

$$\frac{d \ln p}{dT} = \frac{Hv}{RT^2}$$

where

ln p = logarithm to the base e of the vapor pressure
Hv = heat of vaporization, cal./mol.
R = gas constant, 1.987 cal./°C./mol.

Using the equation for the vapor pressure of MCE

$$\log p = 8.305^{b} - \frac{2820}{T}$$

or

$$\ln p = 2.303 \left(8.305^{b} - \frac{2820}{T}\right)$$

$$\frac{d \ln p}{dT} = 2.303 \times \frac{2820}{T^2} = \frac{Hv}{RT^2}$$

$$Hv = 2.303 \times 2820 \times R = 12{,}900 \text{ cal./mol.}$$

and the heat vaporization per gram = 12,900 ÷ 162.3 = 79.6 cal./gram.

It will be noted that these are the average values of heat of vaporization over the range of the experimental data.

3.3.2 Density of Pure and Crude MCE

The density of both the pure MCE and the crude MCE from the 250-kg. bomb was measured at various temperatures by dilatometer. The values are given in Table 4. Also included are the values for the percent expansion from various temperatures to 65 °C., for use in filling calculations. The plot of density versus temperature was linear over the range studied.

[b] This value is incorrectly listed as 8.307 in TDMR 1094, but in Notebook 2363, Harris correctly lists it as 8.305.

Table 4. Density of Pure and Crude MCE

Temp.	Pure MCE (Sample M1067)			Crude MCE (From 250-kg. bomb)		
(°C.)	Exptl. Values (g./ml.)	Values from Plot (g./ml.)	Expansion* to 65 °C. (%)	Exptl. Values (g./ml.)	Values from Plot (g./ml.)	Expansion* to 65 °C (%)
–10		1.105	6.66		1.118	6.48
0		1.096	5.79		1.109	5.62
10	1.0869 (9.8 °C)	1.087	4.92	1.1001 (9.8 °C)	1.100	4.76
15		1.082	4.44		1.095	4.29
20		1.077	3.96		1.091	3.90
25	1.0731 (24.9 °C)	1.073	3.57	1.0864 (24.9 °C)	1.086	3.43
30		1.068	3.09		1.082	3.05
35	1.0636	1.064	2.70	1.0771	1.077	2.57
65		1.036	–		1.050	–

*These values are reliable to two significant figures.

3.3.3 Freezing Point

The freezing point of two samples of MCE was determined by Beckmann technique using a toluene-filled thermometer which was correct at –45.2 °C. (f.p. of monochlorobenzene). Each determination was run in duplicate. It was found that the material was difficult to freeze unless a few particles of a drying agent (Drierite) were added. The values obtained were as follows:

Sample	Freezing Point Obtained	Average Freezing Point
M1078	–51.0; –50.8	–50.9 °C.
S-184	–50.0; –50.0	–50.0 °C.

The Sample S-184 seemed to be somewhat more pure, on the basis of the higher freezing point, as well as on the basis of analysis (Table 1).

3.3.4 Viscosity

The viscosity of pure MCE was measured by Cannon-Fenske-Ostwald viscometer, at various temperatures. The experimental values are given in Table 5. Each value is the average of 3–5 separate determinations:

Table 5. Viscosity of Pure MCE

Temperature (°C.)	Viscosity	
	Centistokes	Centipoises
10.0	3.00	3.26
25.0	2.19	2.35
35.0	1.67	1.78

3.3.5 Surface Tension

The surface tension was determined on pure sample M1081 using a du Nouy interfacial tensiometer calibrated by the method of Macy (*3*). The values were found to vary little with temperature, as follows:

Temperature	Surface Tension
25.0 °C.	32.0 dynes/cm.
30.0 °C.	31.8 dynes/cm.

4. DISCUSSION

The parachor of MCE was calculated from the density and surface tension. In effect, this constant is a corrected molar volume =

$$P = MS^{1/4} = \frac{\text{molecular weight}}{d} S^{1/4}$$

where

P = Parachor
M = molar volume
S = surface tension, dynes/cm.
d = density g./ml.

The value calculated for MCE using the values of d and S at 25 °C. was 359.8. The calculated value using Parachor equivalents tabulated by Glasstone (*4*) and Mumford and Phillips (*5*) was 367.3. The agreement was fair and so confirms the known structure of the material.

The refractive indices were determined on these samples by the Analytical Branch, as a control property. The values at 20 °C. for the sodium D line were in good agreement (Table 1) for all the samples, giving an average figure of 1.4240. The values at 30 °C. were discordant due to difficulties of temperature and humidity control.

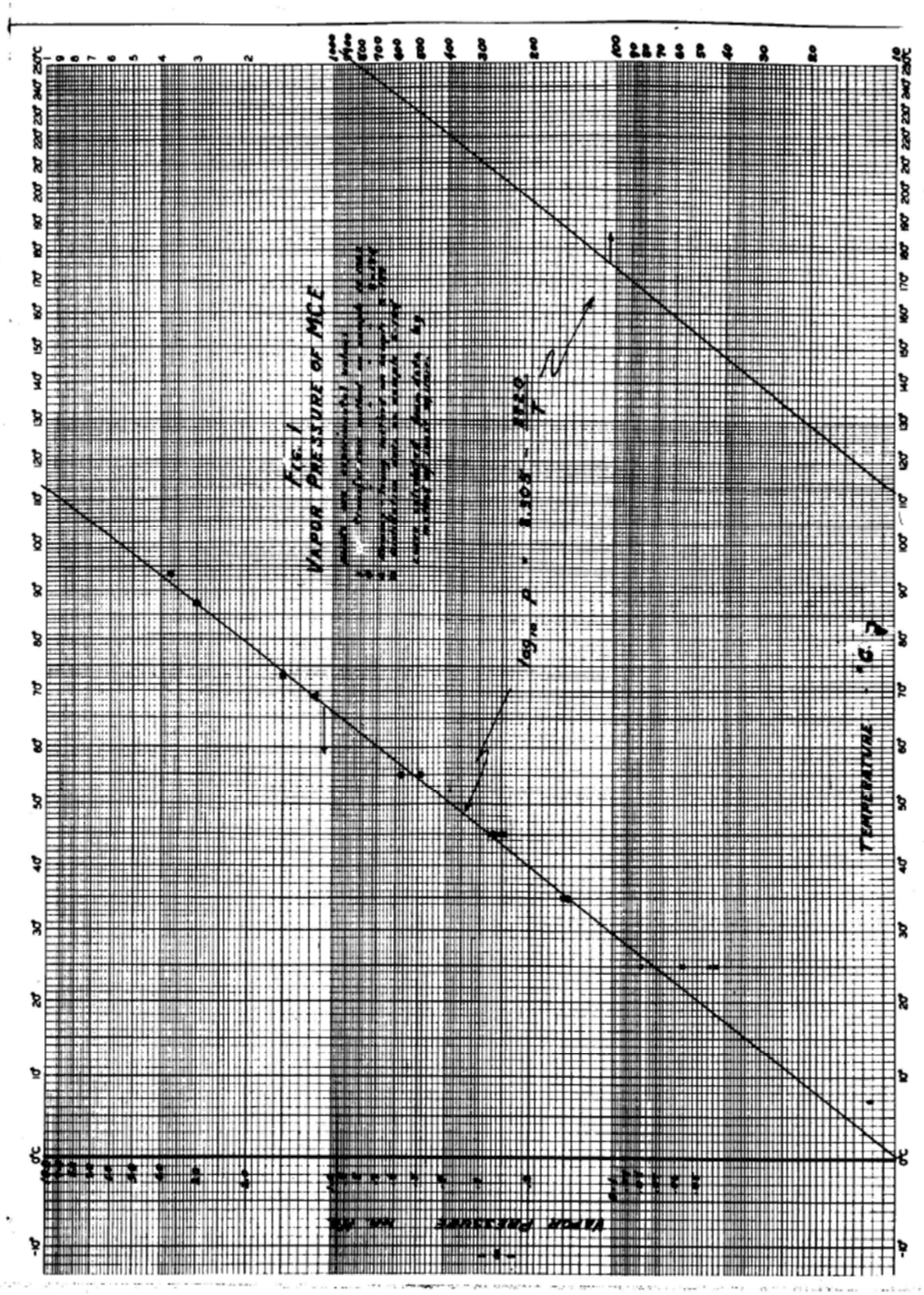
5. CONCLUSIONS

None.

6. RECOMMENDATIONS

None.

Figure. Vapor Pressure of MCE.



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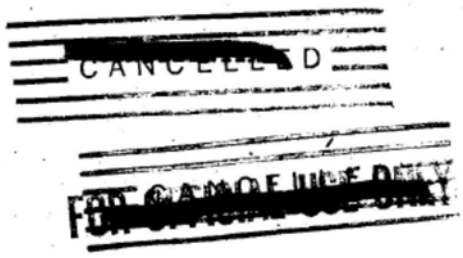

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